

# COATINGS. ENAMELS

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## IMPROVEMENT OF THE TECHNOLOGY FOR OBTAINING PIGMENT-FREE BRIGHTLY COLORED GLAZES

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A new method of coloring glazes is proposed on the basis of improvements in the technology for obtaining brightly colored glass coatings. The method consists of a complex of physical-chemical processes (adsorption, ion-exchange, and precipitation) which already occur at the stage of preparation of the glaze slips, containing water-soluble salts of variable-valence metals, which imparts intense and uniform color and high-quality to calcined glass coatings.

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Colored glazes have found wide application for decorating ceramic articles of various kinds. The good covering power of such glass coatings is due mainly to the fact that expensive ceramic pigments are introduced into the glaze suspensions. However, color stability cannot always be obtained in this way because of a number of factors:

- the past history of the high-temperature synthesis of ceramic pigments and the different dispersity of their finely ground powders;

- the nonuniformity of the distribution of the pigment particles in the glaze suspensions;

- the different resistance of pigments to the corrosive effect of glaze melts which is due to their acid-base properties and the calcination temperature and time used for the glass coatings.

These drawbacks can be avoided by using water-soluble salts of variable-valence metals as the coloring components of the glazes. The technology of ionic coloring of a glass layer is based on the adsorption and ion-exchange processes occurring at the stage when the glaze slip is prepared (during grinding and aging).

At the same time this method for obtaining brightly colored glazes presents other difficulties:

- the partial diffusion of the water-soluble salts from the slip into the surface layers of the raw ceramic green material when a glaze suspension is deposited on it; ultimately, this can greatly decrease the color intensity of the calcined glass layer;

the break up of the continuity of the glaze coating as a result of the appearance of a “bunching” defect, which is mainly due to inadequate wetting of the surface layers of the ceramic, which are saturated with ions of the water-soluble pigment salts, by the molten glass.

This can be prevented by a coloring method which we have proposed (USSR Inventor’s Certificate No. 1020405). It consists of adding a water-soluble metal-pigment salt, precipitated beforehand by water-soluble alkali-metal silicates, when the glaze slip is being ground. However, the drawbacks of such a method are the multiple-stage nature of the process used to prepare the colored glaze and high consumption of the water-soluble pigment salts (up to 25 parts by mass) and, therefore, of the precipitating reagents in the form of alkali-metal silicates whose composition is unstable.

This has raised interest in finding a better and simpler method of obtaining an extensive palette of pigment-free colored glaze coatings with high-intensity and uniform coloration combined with lower concentrations of the colorants that are introduced. This was accomplished by using our combined method of coloration, which consists of simultaneous ion-exchange adsorption of the coloring salts on the mineral components of the glaze suspension followed by conversion of the excess salts (which have not been adsorbed and are present in a dissolved form in the dispersion medium) into insoluble carbonates, uniformly distributed over the entire volume of the slip. The latter property prevents diffusion of the water-soluble transition-metal salts into the surface layers of the uncalcined ceramic material and their par-

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TABLE 1

Main components of the glaze slips*	Content in the experimental composition, parts by mass					
	1-1	1-2	2-1	2-2	3-1	3-2
CoSO <sub>4</sub> · 7H <sub>2</sub> O	3.75	3.75	7.50	7.50	11.25	11.25
Na <sub>2</sub> CO <sub>3</sub>	—	0.71	—	2.11	—	3.53

\* 100% base glaze (Ukraine patent No. 74281).

TABLE 2

Experimental composition	Coating color*	Color hue, nm	Color purity, %	Brilliance, %	Exterior appearance of the coating, scale units
1-1	Light blue	482	5	79	4
1-2	Light blue with a violet hue	460	3	85	5
2-1	Blue with a violet hue	470	5	79	4
2-2	Blue with strong violet hue	420	3	87	5
3-1	Dark violet-blue	420	3	80	4
3-2	Same	400	3	90	5

\* Visual assessment.

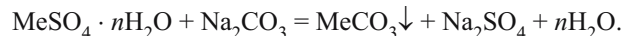
tial removal from the unfritted glaze, which also intensifies the ionic coloring of the calcined glass layer.

The color of the obtained glaze layer depends on the type and quantity of the pigment salt used or on the content of several coloring salts as well as on the mineral and chemical composition of the initial glaze batch (the metal salts were introduced in the form of hydrates).

The content of the free polyvalent-metal salt dissolved in the dispersion medium of the glaze slip was determined by titration [1]. The amount of adsorbed salt, i.e., the part of the salt that is quite strongly bound by the mineral components of the glaze slip, was determined from the difference between the total amount of the colorant added and the amount remaining after titration in the water extract. For example, introducing (parts by mass with 1.0 – 3.0 parts of the corresponding oxide pigment) 3.87 – 11.61 divalent-iron sulfate, 3.75 – 11.25 cobalt (or nickel) sulfate during grinding of unfritted glaze to be deposited on thin ceramic articles, it was

proved experimentally that the amount of salt adsorbed on the mineral components of the base-glaze slip does not depend on its concentration; it is essentially constant and equal to, on average for the suspension studied, about 1.88 parts by mass. A study of glaze slips containing manganese sulfate as the colorant (2.38 – 7.14 parts by mass) established that its adsorption is, on average, 1.47 parts by mass.

On this basis an alkali-metal carbonate was added to the glaze slips. The required amount was calculated according to the chemical equation for the precipitation reaction:



It was determined that when coloring salts are used in the concentrations studied, the equivalent amount of Na<sub>2</sub>CO<sub>3</sub> is, in parts by mass, 0.76 – 3.71 divalent-iron sulfate, 0.71 – 3.53 cobalt or nickel sulfate, and 0.57 – 3.56 manganese sulfate.

No diffusion of the coloring salts into the surface layers of the molded ceramic samples was observed when depositing glaze suspensions prepared in this manner, and the sodium sulfate formed as a result of the precipitation reaction increases in the course of calcination (maximum temperature 1200°C) the brilliance of the glass layer obtained, characterized by high color uniformity and stability. The compositions of the experimental slips and the properties of the glaze coatings obtained using them are presented in Tables 1 and 2.

In summary, our experimental studies have shown that the combined pigment-free method is an expedient way to color glazes. This method consists of an entire complex of processes, involving adsorption, ion-exchange, and co-precipitation of reaction products, in the experimental slips and improves their qualitative, color, and optical characteristics (Ukraine patent No. 74281).

Cobalt-containing glazes obtained by our coloration method are characterized by good continuity, absence of the “bunching” defect, high brilliance (85 – 90%), and higher saturation with blue color, confirmed not only visually but also by colorimetric measurements — a shift of the color hue (420 – 482 nm) into the longer-wavelength range of the visible part of the spectrum (400 – 460 nm).

## REFERENCES

1. F. M. Tulyupa and I. S. Panchenko, *Textbook of Analytical Chemistry* [in Russian], Dnepropetrovsk (2002).